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Study of the absorption edges in $Se_{90}Ge_{10-x}In_x$ chalcogenide glasses

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Abstract : The optical properties of $Se_{90}Ge_{10-x}In_x$ (x = 2, 4 and 6 at.%) have been studied by means of the ultraviolet absorption spectra. The absorption edges are found to be dependent on the indium concentration. Both direct and indirect transitions between valence band and conduction band are found.

Both the optical gap (E_{opt}) and the band width (ΔE) are calculated as a function of indium concentration in the samples. The former decreases while the later increases with the indium concentration. Their values are between 0.32 eV and 2.91 eV.

Keywords : Optical gap, band width, ultraviolet absorption.

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1. Introduction

The study of the optical properties and particularly the absorption edge is a powerful tool for investigating the optically induced transitions, and for providing essential information about the band structure and the energy gap in cystalline and non-crystalline materials.

Analysis of the absorption spectra in the low energy part gives information about the atomic vibration, and that of the higher energy part of the absorption spectra gives knowledge about electronic states in the material.

The UV absorption generally includes the excitation of electrons associated with oxygen anions in glasses. Stevels [1] was the first one to discuss theoretically the ultraviolet absorption mechanism in glasses. Large variations in the values of the band gap of chalcogenide glasses have been shown [2]. Variations in the composition of such materials affect the band gaps [3–5]. The absorption edge of most amorphous semiconductors can be divided into three regions [6].

(i) High absorption region :

It is often observed in semiconducting glass that, at high enough absorption level ($\alpha \geq 10^4$ cm^{-1}), the absorption coefficient $\alpha(\omega)$ has the following frequency dependence :

$$\hbar\omega\alpha(\omega) \sim (\hbar\omega - E_{opt})^r, \tag{1}$$

where r is constant of the order 1, $\hbar = \frac{h}{2\pi}$ where (h) is the Plank constant and E_{opt} is the optical energy gap.

(ii) Exponential region. This region has the following properties

(a) In the absorption coefficient range from 1 cm^{-1} (or less) to about 10^4 cm^{-1}, $\alpha(\omega)$ the absorption coefficient, is described by the formula :

$$\alpha(\omega) \approx \exp(\hbar\omega/E_e) \tag{2}$$

(b) The energy E_e characterizing the slope is almost temperature dependent at low temperatures and has, in many semiconducting glasses, the value between 0.05 eV and 0.08 eV.

(c) At high temperature, the slope decreases with temperature.

(d) In many amorphous semiconductors the regions (i) and (ii) move as a whole.

(iii) Weak absorption tail :

Below the exponential part of the absorption edge an absorption tail is observed. Its strength and shape are found to depend on the preparation, purity and thermal history of the material even if the material is in the bulk form rather than as a film. The absorption coefficient is below 0.5 cm^{-1}. For many materials, the absorption coefficient $\alpha(\omega)$ near the band edge behaves exponentially as a function of photon-energy ($\hbar\omega$) in the form [7] :

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/\Delta E), \tag{3}$$

where α_0 is a constant, and ΔE is the width of the band tails of the localized states in the normally forbidden gap that is associated with the amorphous nature of the materials.

There are two kinds of optical transition at the fundamental edge of crystalline and non-crystalline materials : direct transition and indirect transition. Both kinds of transitions involve the interaction of an electromagnetic wave with an electron in the valence band, which is raised across the fundamental gap to the conduction band. For a direct optical transition from the valence band to the conduction band, it is essential that the wave vector for the electron be unchanged. In the case of indirect transition, the interaction with lattice vibration (phonon) takes place, thus the wave vector of the electron can change in the optical transition and the momentum change will be taken or given up by phonons.

Mott and Davis [8] suggested that the expression for the optical transition can be written as :

$$\alpha(\omega) = B(\hbar\omega - E_{opt})^n/\hbar\omega \tag{4}$$

where B is a constant and n is an index determined by the nature of the electronic transitions during the absorption process. It has been reported [9] that a reasonable fit of equation (4) with $n = 2$ is achieved for many amorphous materials, particularly at the higher absorption values of the edge and suggests absorption by indirect transitions.

Compounds of ZnS, ZnTe, CdTe-ZnTe, ZnS-CdS and ZnS-ZnSe have been of great interest to the scientific community as a potential visible device materials. These materials have excellent luminescent properties, where they are producing high efficiency luminescence under UV and electron beam excitation.

The objective of the present work is to study the optical properties of $Se_{90}Ge_{10-x}In_x$ (x = 2, 4 and 6 at. %). Our results are discussed in the light of the above mentioned approaches.

2. Experimental technique

The alloys were prepared by the melt quenching technique from 99.999 purity Se, Ge and In. The quenching was performed in ice water. The optical absorption data were measured in the wavelength range (200–900 nm) using UV-visible double beam spectrophotometer model Lambda 4B Perkin-Elmer at room temperature. The absorption coefficient $\alpha(\omega)$ was calculated from the relation [10] :

$$\alpha(\omega) = \frac{2.303A}{d},$$

where $A = \text{Ln}(I/I_0)$ is the absorbance, and d is the thickness of the sample.

3. Results and discussion

Figure 1 shows the plot of optical density against wavelength (λ) for $Se_{90}Ge_{10-x}In_x$ glass samples (where x = 2, 4 and 6 at. %). It is clear that there is no sharp absorption edge and

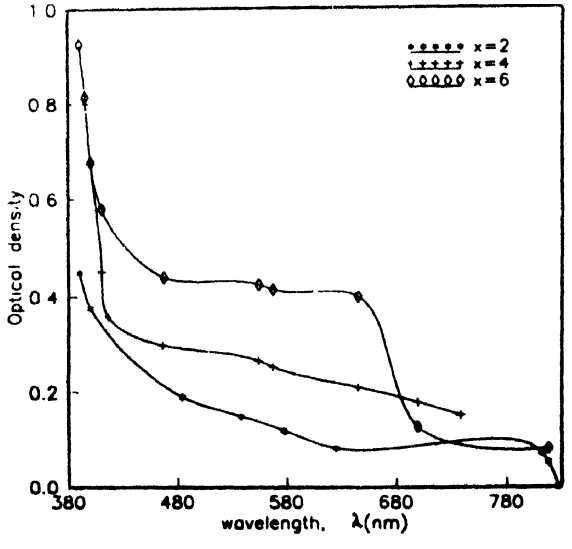

Figure 1. Variation of the optical absorption spectra with wavelength for $Se_{90}Ge_{10-x}In_x$ glasses.

this is a characteristic for the glassy state. The change of absorption edge with the compositions of the studied glasses shows a real shift in the absorption edge to the lower energies. The variation of $(\alpha\,\hbar\,\omega)$ and $(\alpha\,\hbar\,\omega)^{1/2}$ with $(\hbar\omega)$ for the studied glasses are shown in Figures 2 and 3 respectively. As can be seen from these figures, the optical absorption data follow eq. (4) with $n = 1$ and $n = 2$ *i.e.* the optical data could be analyzed in terms of direct and indirect transition.

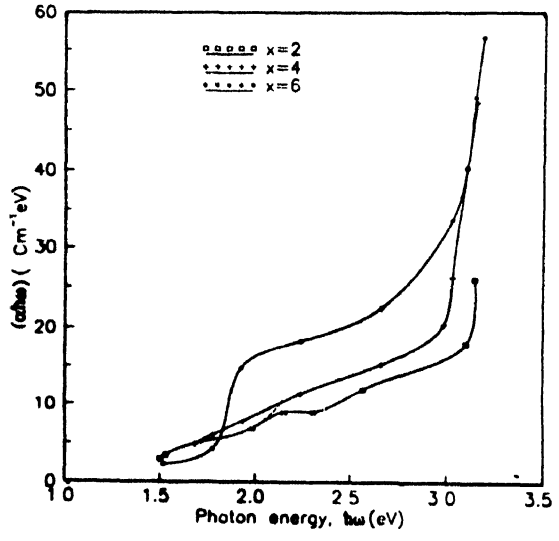

Figure 2. Variation of $(\alpha\,\hbar\,\omega)$ with photon energy $(\hbar\,\omega)$ for $Se_{90}Ge_{10-x}In_x$ glasses.

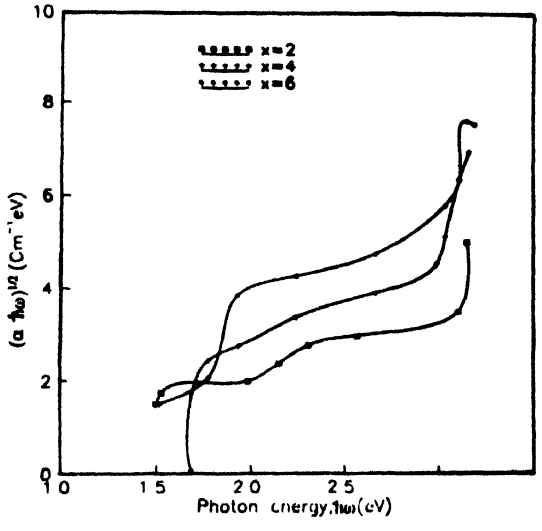

Figure 3. Variation of $(\alpha\,\hbar\,\omega)$ with photon energy $(\hbar\,\omega)$ for $Se_{90}Ge_{10-x}In_x$ glasses.

The values of (E_{opt}) can be obtained from extrapolation of linear part of each curve in Figures (2) and (3) to $(\alpha\,\hbar\,\omega) = 0$ and $(\alpha\,\hbar\,\omega)^{1/2} = 0$. Table 1 shows the $(E_{opt.})$ values obtained from the data by using the least square method.

The plot of E_{opt} against indium concentration in the sample (see Figure 4) showed a linear decrease with increasing values of indium. The density of states model predicts a reduction in E_{opt} with the increase in the degree of disorder in the amorphous phase [11].

Table 1. The effect of indium concentration in the sample $Se_{90}Ge_{10-x}In_x$ on the width of the band tail (ΔE) and the optical energy gap (E_{opt}).

x (at. %)	E_{opt} (eV)		ΔE (eV)
	$n = 1$	$n = 2$	
2	2.9065	2.682	0.3255
4	2.871	1.7053	0.5363
6	1.5108	0.492	1.766

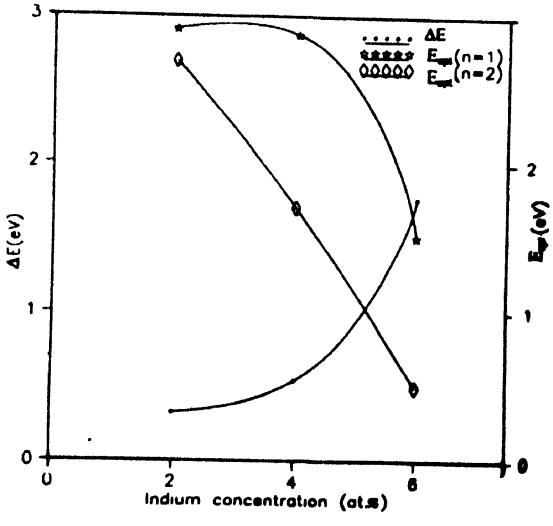

Figure 4. Variation of the band width (ΔE) and the optical gap (E_{opt}) with the indium concentration in the sample $Se_{90}Ge_{10-x}In_x$. for $n = 1$ and $n = 2$ in $(\alpha\hbar\omega)^{1/n}$.

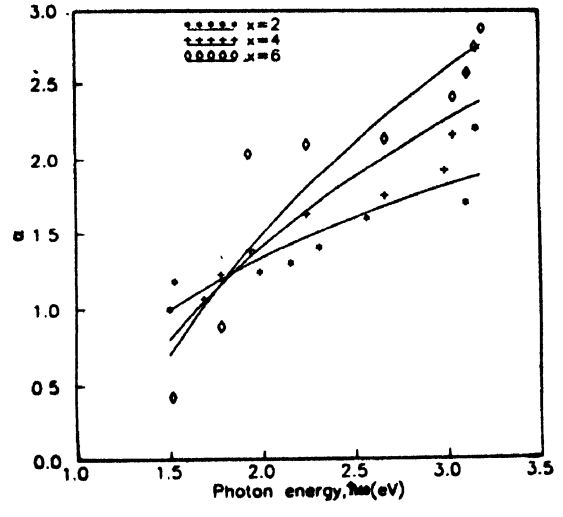

Figure 5. Variation of Ln α (ω) with photon energy ($\hbar\omega$) for $Se_{90}Ge_{10-x}In_x$ glasses.

In the light of this model it is concluded that the increase of indium concentration increases the degree of disorder of the studied glass. This consequently increases the density of states which is confirmed in the next publication [12].

Figure 5 shows the relation between the logarithmic values of $\alpha(\omega)$ and the photon energy ($\hbar\omega$) at different concentrations of indium. From this figure we obtained the values of (ΔE) using eq. (3). The variation of (ΔE) as a function of indium concentration has been shown in Figure 4. As the indium concentration increases, the value of (ΔE) increases.

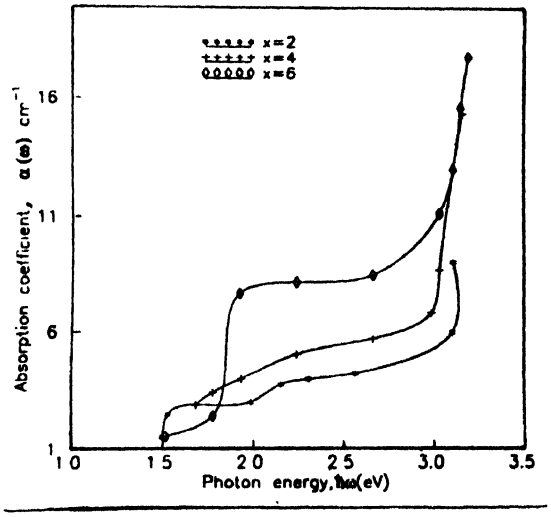

Figure 6. Variation of the absorption coefficient $\alpha(\omega)$ of $Se_{90}Ge_{10-x}In_x$ with photon energy ($\hbar\omega$).

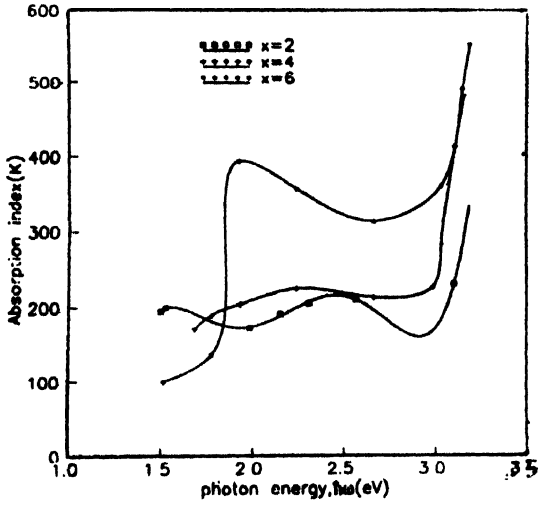

Figure 7. Variation of the absorption index (K) of $Se_{90}Ge_{10-x}In_x$ with photon energy ($\hbar\omega$).

It is also inferred in the density of states model [11] that a decrease in E_{opt} leads to the shifting of the band tailing towards the higher energy regime and hence the value of (ΔE) is expected to increase as a function of indium concentration, as shown in Table 1 and Figure 4. Figures 6 and 7 show the variation of the absorption coefficient $\alpha(\omega)$ and

absorption index (K) as a function of photon energy ($\hbar\omega$) at different concentration of indium.

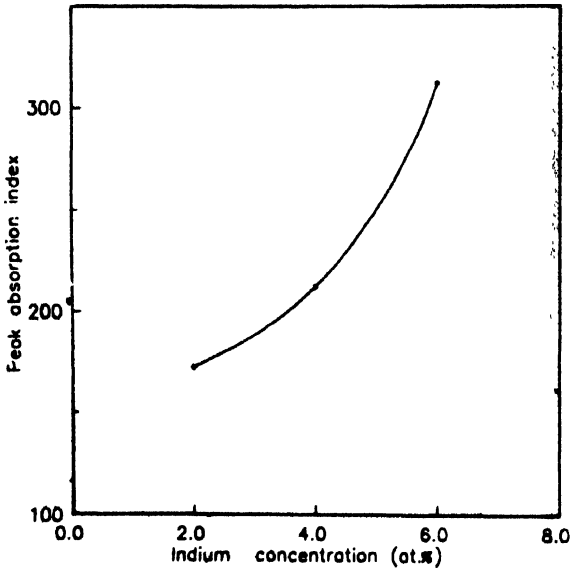

Figure 8. Variation of the peak absorption index with indium concentration in $Se_{90}Ge_{10-x}In_x$ glasses.

A distinct dependence of the absorption index on the indium content in the sample and photon energy is observed. This dependence exhibits peaks around 2.45 eV and the maximum attained is dependent on the photon energy. The obtained peak values of the absorption index (K) are plotted at various indium concentrations in Figure 8.

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